

CARBON BLACK PREPARATION FROM LOW-TEMPERATURE LIGNITE PITCH

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Carbon black consists essentially of finely divided particles of carbon produced by incomplete combustion of carbonaceous fuels, both liquid and gaseous. Carbon black frequently is identified by designating the method of preparation, e. g. channel black, lamp black, furnace black, oil black, and thermal black. Carbon black from the channel, gas, and oil furnace processes is produced by controlled combustion. In the thermal process, carbon black is produced by thermal decomposition of hydrocarbons in the absence of air or flame. Channel black, produced from natural gas, was the main type at the beginning of the carbon black industry (Bond, 1968), but gradual increase in natural gas price impelled the carbon black industry to look for new feedstocks. Now, most carbon black is produced from petroleum-derived feedstock (Drogin, 1968). The carbon industry in the United States is about 100 years old, and more than 135 marketable grades of carbon black meet a wide range of industry specifications (Drogin, 1954).

This paper discusses the preparation, characteristics, and properties of carbon black produced by the thermal decomposition of low-temperature lignite tar pitch. A variety of other carbonaceous materials have been evaluated as carbon black feedstock via thermal decomposition (Kulik, 1961; Williams, 1953; Johnson, 1969).

EQUIPMENT AND MATERIALS

A 13-inch-long section of 6-inch pipe equipped with external electric heaters served as pitch feed tank. A gear pump fed the pitch to the production furnace. The latter was constructed of 10-gauge carbon steel and had two main parts, the firebox and production zone. The firebox was 9 inches in diameter and 9 inches long overall, with downstream end tapered 45° to 3 inches in diameter. Refractory and insulation made the outside dimensions 27 inches in diameter by 18 inches long. The production zone consisted of silicon carbide tube 4 inches in diameter by 36 inches long surrounded by insulating brick. Outside diameter of the production zone was 21 inches.

Two natural gas burners entering the firebox tangentially preheated the furnace and supplied heat during a run.

Attached directly to the discharge end of the furnace was a quenching chamber, 12 inches in diameter and 42 inches long. Initially it was constructed of 12-inch carbon steel pipe, but its corrosion contaminated the product, so it was rebuilt using stainless steel. A water spray quenched the gases and carbon leaving the furnace.

Carbon black was removed by a 12-inch diameter by 42-inch-long knock-out tank made from stainless steel and equipped on the inside with a water spray. Tangential entry of the gas gave cyclone-type action that assisted in removal of carbon black.

The 2-foot-square wet filter was separated into two compartments by a screen which supported filter paper. Both the box and screen were made of stainless steel. The dry filter was a wool-bag type, 4-1/2 inches in diameter by 4 feet long.

Feed material for the study was pitch obtained from tar produced by the Texas Power & Light Company from the carbonization of Texas lignite at 900° F in a fluidized bed by the Parry process (Parry, 1955). The tar was distilled under vacuum to an atmospheric boiling point of 630° F, and the resulting residue amounted to 45% of the tar. Chemical and physical properties of the pitch are given in Table 1.

PROCEDURE

Pitch was placed in the feed tank (Figure 1), melted, heated to about 400° F, and pumped into the preheated furnace. Carbon black formed in the production zone, passed into the quenching chamber where it was cooled by the water spray, and dropped to the bottom. Carbon black remaining in the products of combustion was carried to the knock-out tank for removal by the water spray and cyclonic action. Gas carrying unremoved carbon black then went to the dry wool-bag filter for final cleaning up of the gas, after which the gas was metered, sampled, and vented. Carbon black from the quenching chamber and knock-out tank was collected on a wet filter, from which it was removed, washed, dried, and prepared for testing.

RESULTS

Maximum yields of carbon black at temperatures ranging from 1,800° to 2,500° F are given in Table II and presented in Figure 2. Yields increased from 16.5% at 1,800° F to 37.0% at 2,500° F. Hydrogen content, on the other hand, decreased with increase in temperature. In the 1,800° and 2,000° F runs, corrosion of the carbon steel quenching chamber contaminated the product, as revealed by the high ash and iron content. Ash and iron values dropped significantly in subsequent runs utilizing a stainless-steel chamber. Sulfur content remained relatively constant at 0.7%. A yield of 37% represents 40 pounds of carbon black per ton of lignite carbonized.

Electron micrographs of the carbon black are shown in Figures 3 and 4. These blacks were produced at about 2,300° F. The particles appear spherical in shape, range from 200 to 3,000 Å in diameter, and have a tendency toward arrangement into chainlike structures. Blacks in which this effect is prominent are generally referred to as structure blacks. A high degree of structure is usually indicative of high electrical conductance. These electron micrographs look much like those from a typical SRF material (Kirk and Othmer, 1949). The tendency to form chains also indicates that the particles will bind well with the matrix in compounding.

Results of tests and compounding of the carbon black compared with a commercial-type SRF carbon black, are given in Table III. CB-12 designates a carbon black produced at 2,450° F; CB-13A at 2,250° F; and CB-3, at 2,000° F. Carbon blacks from lignite pitch were intermediate in fineness to thermal and SRF type carbons, but of higher chain structure. They also differed in tinting strength, but this estimate of fineness correlated only roughly with tensile strength of the vulcanizates. Oil absorption (shape factor) of the carbon black was much higher than for furnace black, indicating nonspherical particles. Vulcanizate viscosity and modulus data agreed directionally with oil absorption when related to furnace black data.

The lignite-derived carbon black was high in ash and very high in iodine number. Iodine number does not appear to be a measure of surface area for these samples. Both the high iodine number and oil absorption could be influenced by the high volatile content of the samples and not be a true indication of surface area and particle shape.

The samples dispersed well in rubber. The tensile strength was equivalent to or lower than for furnace black. The CB-13A run appears to be coarsest and gave lowest tensile. The blend of CB-12 and CB-3 was intermediate. Two of the samples produced compounds higher in tensile modulus, dynamic modulus, and hardness than furnace black. This indicates nonspherical particles as confirmed by the higher oil absorption. The mechanical properties of the experimental compounds were similar to those of furnace black. Run CB-12 compound was highest in damping and heat buildup and lowest in resilience.

The compounds differed only slightly in scorch time. The coal derived samples resulted in compounds of a faster cure rate than furnace black.

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Table I. Properties of Lignite Pitch

| | |
|--|-------|
| Flash point, ° F | 510 |
| Softening point (r&b) glycerol, ° F | 194 |
| Softening point (cube in glycerol), ° F | 221 |
| Penetration at 77° F, 100 grams, 5 seconds | 0 |
| Specific gravity, 25° C/25° C | 1.128 |
| Ash | 0.35 |
| Water | 0.00 |
| Ductility, cm at 77° F | 0 |
| Bitumen, soluble in CS ₂ | 78.80 |
| Free carbon | 20.85 |
| Conradson carbon | 20.81 |
| Distillation to 572° F (ASTM D2569-67) | 6.40 |
| Softening point of residue (r&b), ° F | 194 |
| Sulfonation index of distillate to 572° F | 0 |

| Ultimate analysis | <u>Percent</u> |
|--------------------|----------------|
| Carbon | 84.72 |
| Hydrogen | 8.53 |
| Nitrogen | 0.87 |
| Oxygen | 4.62 |
| Sulfur | 0.90 |
| Chlorine | 0.01 |
| Moisture | 0.00 |

Table II. Carbon Black Yields and Composition

| Temp., ° F | Pitch fed, lb | Carbon Black Yield | | Carbon black composition (wt-%) and properties | | | | | | | |
|---------------|------------------|-----------------------|--------------------------|--|----------------|-----|------|-----|----------------------------|------------------|------------------------------|
| | | Weight, lb | Proportion of feed, % | Carbon | H ₂ | Ash | Fe | S | Oil absorption, ml/g | Iodine number | Particle size, microns |
| 1800 | 0.8 | 0.13 | 16.3 | 85.77 | 1.80 | 6.2 | 1.55 | 0.8 | | 32 | 0.02-0.20 |
| 2000 | 2.0 | 0.5 | 25.0 | 89.42 | 1.73 | 2.3 | 0.66 | 0.6 | | | 0.02-0.15 |
| 2250 | 5.6 | 1.6 | 28.6 | 95.47 | 1.00 | 0.4 | 0.07 | 0.7 | 0.53 | 18 | |
| 2350 | 8.2 | 2.7 | 33.0 | 95.25 | 1.27 | 0.6 | 0.07 | 0.7 | 0.81 | 20 | 0.02-0.30 |
| 2500 | 4.6 | 1.7 | 37.0 | 94.96 | 0.89 | 0.7 | 0.07 | 0.7 | 0.56 | 19 | 0.02-0.15 |

Table III. Carbon Black and Rubber Properties

| Carbon | Run CB-12 | Run CB-12 + CB-3 | Run CB-13A | Commercial furnace black |
|---------------------------------|-----------|---------------------|------------|--------------------------------|
| Carbon Black Properties | | | | |
| Tinting strength | 33 | 16 | 12 | 24 |
| Oil absorption, gal/100 lb | 12.8 | 15.8 | 10.2 | 4.4 |
| Iodine number, mg/g | 32 | 12 | 45 | 10 |
| Volatile content, wt % at 1750° | 7.9 | 13.4 | 14.5 | 0.1 |
| Ash, wt % | 0.89 | 2.4 | 0.74 | 0.03 |
| Rubber Properties | | | | |
| 20' L-300 | 110 | 90 | 40 | 50 |
| 20' Tensile | 530 | 520 | 210 | 300 |
| 60' L-300 | 700 | 640 | 390 | 410 |
| 60' Tensile | 1770 | 1450 | 1180 | 1510 |
| 60' Elongation | 720 | 600 | 740 | 700 |
| 60' Shore hardness | 55 | 53 | 48 | 47 |
| 100' tensile | 1580 | 1320 | 940 | 1380 |
| Max. tensile | 1780 | 1580 | 1180 | 1710 |
| Visual dispersion | 4.0 | 4.5 | 3.9 | 4.5 |
| Dynamic Properties | | | | |
| Complex modulus | 93.0 | 88.2 | 76.8 | 75.0 |
| Viscous modulus | 15.0 | 12.8 | 12.0 | 11.0 |
| Phase angle | 9.3 | 8.3 | 9.0 | 8.5 |
| Resilience, % | 59.7 | 63.1 | 60.8 | 62.4 |
| Goodrich heat buildup | 97 | 89 | 82 | 88 |
| Rheometer Cure Properties | | | | |
| Minimum torque | 2.6 | 2.2 | 2.0 | 2.0 |
| Maximum torque | 63.0 | 62.1 | 52.0 | 52.9 |
| Time to 7# rise | 10.8 | 10.7 | 11.2 | 10.7 |
| Time to 90% max. torque | 31.4 | 31.8 | 28.2 | 36.3 |
| Cure rate | 7.4 | 7.1 | 6.4 | 4.8 |

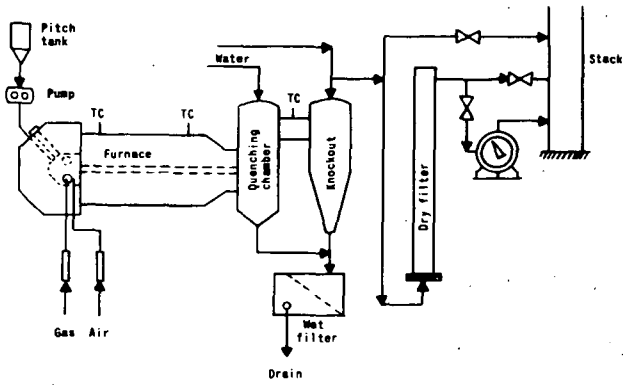


Figure 1. - Carbon Black System.

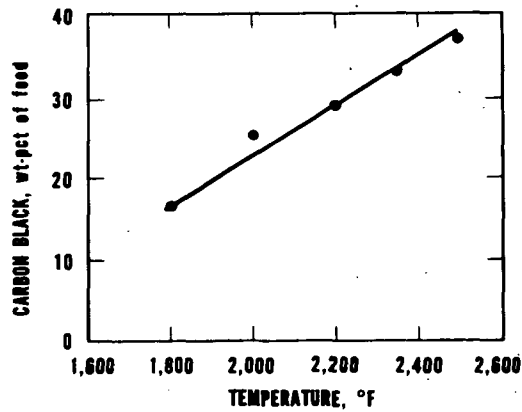


Figure 2. - Carbon Black Yields Versus Temperature.

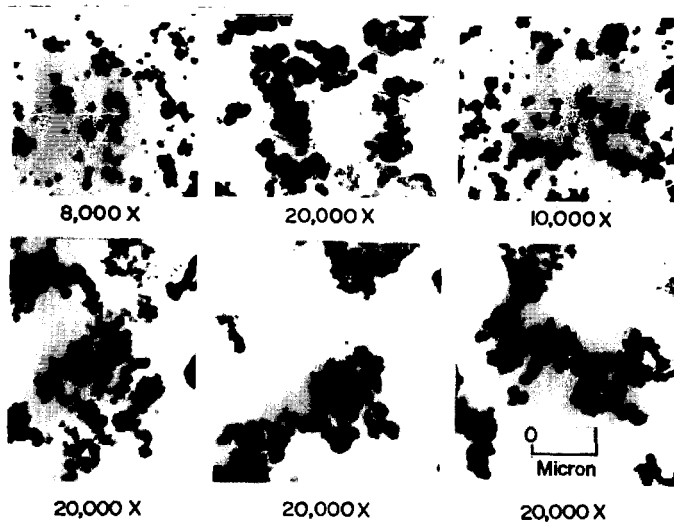


Figure 3. - Electron Micrographs of Carbon Black from Low-Temperature Lignite Pitch.



Figure 4. - Electron Micrograph of Carbon Black.